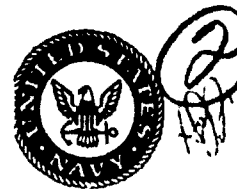


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Water Adsorption on Diamond (110) Studied by Multiple Internal Reflection Infrared Spectroscopy

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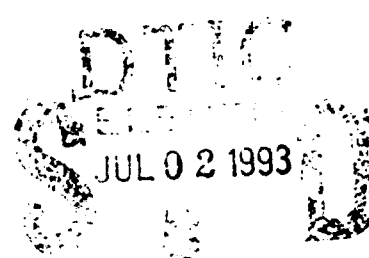
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June 14, 1993

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13. ABSTRACT (Maximum 200 words) The adsorption of water on a natural, type IIa diamond (110) surface is studied by multiple internal reflection infrared spectroscopy (MIRIRS). Similar results are observed for the hydrogen-free, and hydrogen-terminated diamond (110) surfaces. Exposure of water at 100 K reveals the presence of physisorbed molecular water on the surface, with no evidence of dissociation. Upon heating to approximately 160 K, the water is desorbed from the surface without any evidence of chemisorption or decomposition. Exposure of the surface to water at elevated temperatures (373 and 773 K) also failed to produce any evidence in the infrared spectra of chemisorption or decomposition. However, the absence of water dissociative chemisorption may be the result of sp ² carbon contamination which was found on the surface at the conclusion of the experiments.				
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WATER ADSORPTION ON DIAMOND (110) STUDIED BY MULTIPLE INTERNAL REFLECTION INFRARED SPECTROSCOPY

Introduction

The growth of diamond by chemical vapor deposition (CVD) has received considerable attention recently because of the diverse technological applications that can exploit the superb properties of this material as well as the many unanswered scientific questions about the manufacturing process. [1]. As a result, much effort has been devoted to trying to understand the diamond growth process, to improve and control its quality, to increase growth rates, to achieve diamond growth at lower substrate temperatures, and to reduce the costs of manufacture and fabrication.

The growth of diamond [2] on non-diamond substrates was first carried out using a dilute mixture of CH_4 in H_2 in an environment, such as a plasma or hot filament, capable of producing atomic hydrogen and carbonaceous radical species. However, due to the quasi-equilibrium established in the gas phase, diamond growth is relatively insensitive to the choice of hydrocarbon in the feed gas [1, 3, 4]; only the overall C:H ratio and the degree of hydrogen dissociation are important [5, 6]. The principal effects of H atoms during growth are to stabilize the surface carbon atoms in sp^3 hybridization, etch surface sp^2 bonded carbons, and abstract the surface-terminating hydrogens to make reactive surface sites [5]. Addition of other species to the growth environment, such as oxygen, water, or alcohols [7-16], and halogens [17, 18], can form species which function like H atoms, e.g., O, OH, F, Cl, etc., which are advantageous to diamond growth.

The addition of water or other oxygen-containing species to the growth environment improves film quality, increases growth rate, and allows diamond deposition at lower substrate temperatures [7-16]. A number of explanations have been proposed to explain this effect. For example, oxygen can produce OH or other radical species which preferentially etch the non-diamond carbon in the growing film [8, 19, 20]. Oxygen may also decrease the formation of non-diamond carbon by reducing the concentration of polyacetylenic or aromatic species in the gas phase, thus decreasing condensation on the surface [21-23]. Oxygen may also enhance the formation of methyl radicals or other precursors necessary for diamond growth [24]. Finally, oxygen may promote diamond growth by creating a more reactive surface, for example, by increasing the number of vacant surface sites.

Currently, little is known about how oxygen-containing species interact with the diamond surface. Molecular oxygen reacts with diamond at elevated temperatures (973 - 1173 K) to produce gas phase CO and CO_2 [25, 26]. More recently, it has been shown that atomic oxygen sticks readily on both the clean and H-terminated surface to produce a stable oxygenated layer, which desorbs as CO and CO_2 upon heating to 873 K [27]. However, little is known about how water and OH species interact with the diamond surface. Struck and D'Evelyn [28] exposed a C(100) surface to water as they cooled the surface from either 1070 or 1400 K to room temperature and observed ether (C-O-C), hydroxyl (C-OH), and carbonyl ($>\text{C}=\text{O}$) vibrational modes on the surface with infrared multiple internal reflection spectroscopy.

In this paper, multiple internal reflection infrared spectroscopy (MIRIRS) is used to determine the role of water in diamond chemical vapor deposition. Water adsorption on hydrogen-free, H-terminated, and 'graphitized' (a surface with significant pi-bonded carbon composition) diamond(110) surfaces were examined.

Experiment

The experiments were carried out in a two-level UHV chamber, shown schematically in Fig. 1, equipped with differentially pumped KBr windows for transmission of the infrared beam and a mass spectrometer for residual gas analysis. The chamber was pumped by a 140 l/s ion pump and had a base pressure of 7×10^{-10} Torr.

The crystal used for these studies was a natural, type IIa, diamond multiple internal reflection element which is trapezoidal in shape and measuring 11 mm long x 5.5 mm wide x

0.71 mm thick, gives 15 internal reflections at 45° . The large parallel faces of the sample were found by Laue x-ray diffraction to be oriented within 7° of the (110) direction. The entrance and exit faces for the light were nominally of (100) orientation. Prior to insertion in the chamber, the sample was cleaned in a series of boiling acid mixtures (1:3 mixture of HNO_3 and HCl followed by a 3:2 mixture of H_2SO_4 and HNO_3) and then rinsed with distilled water, acetone and methanol. Based on integrated X-ray photoelectron spectroscopy (XPS) elemental peak areas, this surface treatment produces oxygen concentrations of 5-10 % averaged over an approximately 50Å sampling depth [29] which corresponds to a 0.5 monolayer coverage of oxygen. At the conclusion of this series of experiments, a single-pass cylindrical mirror analyzer (CMA) became available and was added to the apparatus. The condition of the diamond surface was examined using Auger electron spectroscopy (AES) and electron energy loss spectroscopy (ELS) while the crystal temperature was held at approximately 770 K. Auger spectra were taken with a focussed 3 keV electron beam with an electron gun emission current of < 0.1 mA. The electron loss spectrum was acquired with a beam energy of 149 eV. The current at the crystal was not determined for either measurement. Both the C KLL Auger lineshape and ELS (Fig. 2) indicated the presence of graphitic (sp^2 hybridized) carbon at the conclusion of the MIRIRS experimental series.

The diamond was mounted in the chamber on a liquid nitrogen cooled manipulator. The crystal was suspended between thin tantalum wires and held along opposite edges by small tantalum clips, as shown in the inset in Fig. 1. The mounting scheme minimized the area of the light-reflecting faces covered by the mount. Since the light sampled both the front and back faces of the crystal, clamping the crystal onto a heater block was impossible. The crystal was heated resistively by passing current across the tantalum support wires with a Sorenson DCS 20-50 programmable power supply. The crystal temperature was maintained by controlling the DC power supply with an LFE model 3000 PID temperature controller while the crystal temperature was monitored by a chromel-alumel thermocouple spot-welded to one of the tantalum clips. This control system allowed the crystal temperature to be heated linearly from 95°K to greater than 1323°K , and was able to maintain a constant (± 0.5 K), reproducible crystal temperature during each infrared measurement.

The infrared spectra were collected with a Nicolet 800 FTIR spectrometer using a broad band MCT detector having a D^* of $4 \times 10^9 \text{ cm Hz}^{1/2} / \text{W}$. The optical layout is schematically illustrated in Fig. 1. The collimated infrared beam from the spectrometer was reflected from two flat mirrors and then focused with a 16" focal length spherical mirror through one of the KBr windows onto the entrance face of the diamond MIR element. After traveling through the crystal, the infrared beam exited the chamber via another KBr window and was focused onto the detector with an elliptical mirror. The entire beam path outside of the vacuum chamber was purged with dry nitrogen. The single beam infrared spectra reported here are an average of 2000 scans taken at 8 cm^{-1} resolution and 20 KHz scanning speed. This yields a data collection time of about 15 minutes for each spectrum. All spectra were collected at a sample temperature of 100 K after higher temperature treatments of the surface.

The surface was exposed to water by backfilling the chamber via a leak valve with 5×10^{-9} to 1×10^{-8} Torr of water vapor. The water used for the experiment was triply-distilled, electrochemistry grade water, which was degassed of residual air by three freeze-pump-thaw cycles. The glass and metal water bulb was connected to a leak valve via an all stainless steel vacuum line which was evacuated and baked prior to being filled with water vapor.

Water adsorption was examined on the diamond (110) surface under two different surface conditions. The first surface condition, which will be referred to as the clean surface, was generated by annealing the crystal at 1323 K for 1 minute. Photon stimulated ion desorption (PSID) measurements [29] indicate that this treatment produces a relatively hydrogen-free surface i.e. hydrogen-deficient, surface. After annealing C(110) to about 1123-1173 K, Pepper [31] found that a surface electronic state appears on the clean surface which disappears upon exposure to atomic hydrogen. Recent temperature programmed desorption measurements by

Russell, et.al. [32], indicate hydrogen recombinative desorption on the C(110) surface is complete by 1300 K. The second surface condition, which will be referred to as the H-terminated surface, is prepared by exposing the "clean" surface at 400°C (673 K), to at least 1000 Langmuirs of H₂ (Spectra Gases, 99.9999% pure) at 5×10^{-6} Torr in the presence of a hot (1723 K) tungsten filament which is located about 2 inches from the crystal. This treatment is thought to saturate the surface with hydrogen. Prior to the H atom dosing, the hot tungsten filament was degassed of volatile contaminants by heating to 2000 K with the diamond surface out of the line-of-sight of the filament. Using temperature programmed desorption (TPD), Russell, et.al. [32] found that a C(110) could be saturated with hydrogen using this surface treatment. At the conclusion of the experiments, evidence of sp² carbon contamination was observed on the surface by Auger electron spectroscopy (AES) and electron loss spectroscopy (ELS). It is not known whether this contamination occurred gradually during the course of the experiments or was present for all of the results described here. When polycrystalline diamond surfaces are heated, gradual contamination of the diamond surface with sp² hybridized carbon was observed [33] by ELS and high resolution electron energy loss spectroscopy (HREELS).

Results

A typical single beam spectrum collected through the diamond MIR (Fig. 3) reveals that there are two usable spectral regions for the MIR experiment: one from about 450 cm⁻¹ to 1750 cm⁻¹ and another from 2600 cm⁻¹ to about 7200 cm⁻¹. Because of the long optical path length through the crystal, even weak absorptions can significantly attenuate the transmitted light. In the region from about 1750 cm⁻¹ to 2600 cm⁻¹, all the light is absorbed due to the two-phonon absorption of the diamond, making this region unusable for MIR. In addition, some three-phonon absorption by the diamond is also observed in the regions around 3200 cm⁻¹ and 3600 cm⁻¹, resulting in reduced sensitivity in these regions.

The MIR spectra for a series of six different water vapor exposures (0.4 - 5.0 L) on the hydrogen-free diamond(110) are shown in Fig. 4. The crystal surface temperature was held at 100 K during the water exposures and the collection of the infrared spectra. A similar series of spectra for the H-exposed surface are shown in Fig. 5. There are four absorption bands in these spectra: one band at 680-780 cm⁻¹, another at 1620 cm⁻¹, and two overlapping bands at 3200 to 3400 cm⁻¹. Upon heating the crystal to about 160 K, all four absorption bands disappear and no new bands are observed, suggesting that the species on the surface simply desorb from the surface upon heating to 160 K. This desorption temperature is consistent with recent temperature programmed desorption measurements of water on C(110) [34]. Exposure of the clean surface to 1 L of water at elevated (either 373 or 773 K) surface temperatures, either with or without a hot iridium filament (1100°C exposed to only one side of the crystal) failed to produce any observable bands in the MIR spectra.

Discussion

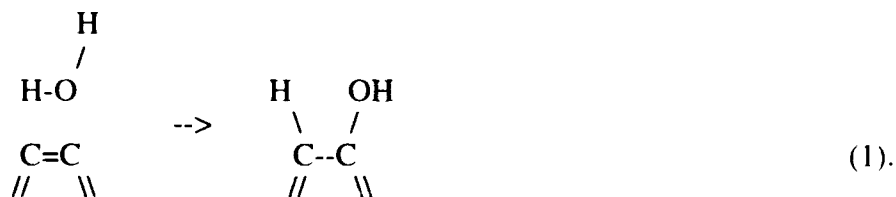
Based on the IR spectra of water on other surfaces and bulk ice [35,36], we assign the observed IR bands of molecular water condensed on the diamond (110) surface as follows. The band at 680-780 cm⁻¹ is assigned to the librational (frustrated rotation) of condensed molecular water [35]. The 1620 cm⁻¹ mode is assigned to the H-O-H bending mode of condensed water, and the two overlapping modes in the 3200-3400 cm⁻¹ are assigned to the symmetric and asymmetric O-H stretching modes for hydrogen-bonded O-H species [35]. The presence of the H-O-H bending mode at a frequency very close to that of bulk ice, the low desorption temperature of the species from the surface, and the lack of absorption modes in the C-O stretching region (1000 to 1100 cm⁻¹) all suggest that the water is simply physisorbed on the

diamond surface for both the H-exposed and clean diamond(110) surfaces. To the limits of our detection, no evidence of chemisorption or dissociation of water is observed. Even at the lowest water coverages at 100 K, hydrogen-bonded O-H stretching modes are observed. This indicates that water forms islands on the diamond surface at low coverages, and is consistent with the conclusion that water simply physisorbs on the diamond surface. The hydrogen bonding tendency of water molecules can easily overcome the small barrier to diffusion of water molecules across the surface [35]. This results in islanding, a common behavior for low coverage physisorbed water.

The observation of water island formation on a hydrogen terminated diamond surface is consistent with measurements and calculations which have been made on an analogous surface, methyl-terminated self-assembled n-alkanethiol monolayer films. Nuzzo, et al. [36] recently examined water adsorption on methyl-terminated surfaces by single-reflection infrared spectroscopy over a range of temperatures. They observed a temperature dependence in the OH stretching region of the spectrum which was related to the structure of the water overlayer. They were able to distinguish polycrystalline ice from amorphous water. By heating the surface, they observed the transition from one phase into another. One point to note is that even at low (submonolayer) water coverages, the structure of water on the surface was that of polycrystalline ice. The spectra of water overlayers produced in this study were similar to the amorphous water spectra of Nuzzo et. al.[36]. Dubois, et.al. [38] in their study of the kinetics for water desorption from a methyl-terminated self-assembled monolayer film, found that even at low submonolayer water coverages, the desorption kinetics were zero order, consistent with islanding of the water molecules on this hydrophobic surface. The leading edge of the thermal desorption curves undercut each other with increasing initial surface coverage. This behavior was attributed to strong hydrogen bonding between the water molecules. Recent molecular dynamics simulations [37] of the interaction of water with methyl-terminated self-assembled monolayers found that water would ball-up into a cluster on this hydrophobic surface with a surface contact angle in good agreement with experimental measurements.

While one might expect only physisorption of water on the hydrogen-terminated diamond surface, it is somewhat surprising that the water does not seem to chemisorb or dissociate on the clean diamond(110) surface upon exposure at elevated temperature (373 or 773 K) or upon heating the surface exposed at 100 K. On silicon and germanium surfaces, water dissociatively chemisorbs into H and OH species upon exposure at room temperature and also upon warming a surface which has been exposed to water at low temperatures [40-46]. Although the initial sticking coefficients for water on many of the low index planes of silicon and germanium are rather low at 300 K, it appears that water physisorbed on these surfaces at low temperatures has a high probability of dissociation upon warming to 300 K. We were not able to achieve dissociative chemisorption of water using this procedure. Struck and D'Evelyn [28] dissociatively chemisorbed water on C(100) when they exposed the surface to 1×10^{-7} Torr of H₂O while cooling from either 1070 or 1400 K to room temperature. They speculated that water chemisorption occurred as the sample temperature cooled below the desorption threshold of oxygen adsorption products. On C(100) the products of oxygen adsorption, CO and CO₂, desorb around 870 K [39].

The absence of dissociative chemisorption of water on C(110) may be due to several reasons. It is possible that the diamond(110) surface is particularly inert when interacting with water because of a difference in surface structure. Struck and D'Evelyn [28] postulate the water interacts via the following mechanism on C(100):



Perhaps the required double bonded site is not present on the hydrogen-free diamond (110) surface. Another explanation is that dissociative chemisorption of water occurs above 773 K, temperatures not examined in this work. We cannot exclude the possibility that the amount of chemisorption/dissociation on this surface was below the limits of our detection. On the silicon(110) and Ge (110) surfaces at 300 K, the saturation coverage of water is roughly 1/4 [45], and 1/6 monolayer [40], respectively. Struck and D'Evelyn did not determine the coverage of chemisorbed water on the C(100) surface. In terms of the diamond growth environment, our results imply that reaction of molecular water with the diamond (110) surface is unimportant, however it is still possible that OH species may play a role, for example, by abstracting hydrogen from the surface to create vacant sites or reacting with other crystallographic planes. This possibility will be investigated.

The results and conclusions regarding the reactivity of water on the hydrogenated and hydrogen-free diamond surface are not conclusive because, at the end of the experimental series, the diamond surface was found to be graphitized (rich in sp^2 hybridized carbon). When this graphitization occurred is not known. Therefore, we cannot exclude the possibility that the sp^2 carbon contamination prevented dissociative chemisorption of H_2O . The observation of sp^2 carbon contamination occurred just prior to removal of the borrowed MIRIRS crystal for return to its owner and precluded further experiments with it. The reactivity of water on diamond at surface temperatures greater than 773 K and with varying degrees of graphitization will be explored with a new diamond MIR element. AES and ELS measurements will be integrated throughout the entire experimental series.

Conclusions

Water physisorbs on both the hydrogen-free and hydrogen-terminated diamond(110) surfaces at 100 K and desorbs from the surface upon heating to approximately 160 K. No evidence of water chemisorption or dissociation is observed upon exposure of the clean diamond(110) surface at 300 K or 773K to water, or upon warming the surface which was exposed to water at 100 K. These results suggest that dissociative chemisorption of water on diamond, if it does occur, occurs at surface temperatures above 773 K. However, at this time, we cannot exclude the possibility that sp^2 carbon contamination inhibited the dissociative chemisorption of water on the diamond MIR element throughout the experimental series.

Acknowledgements

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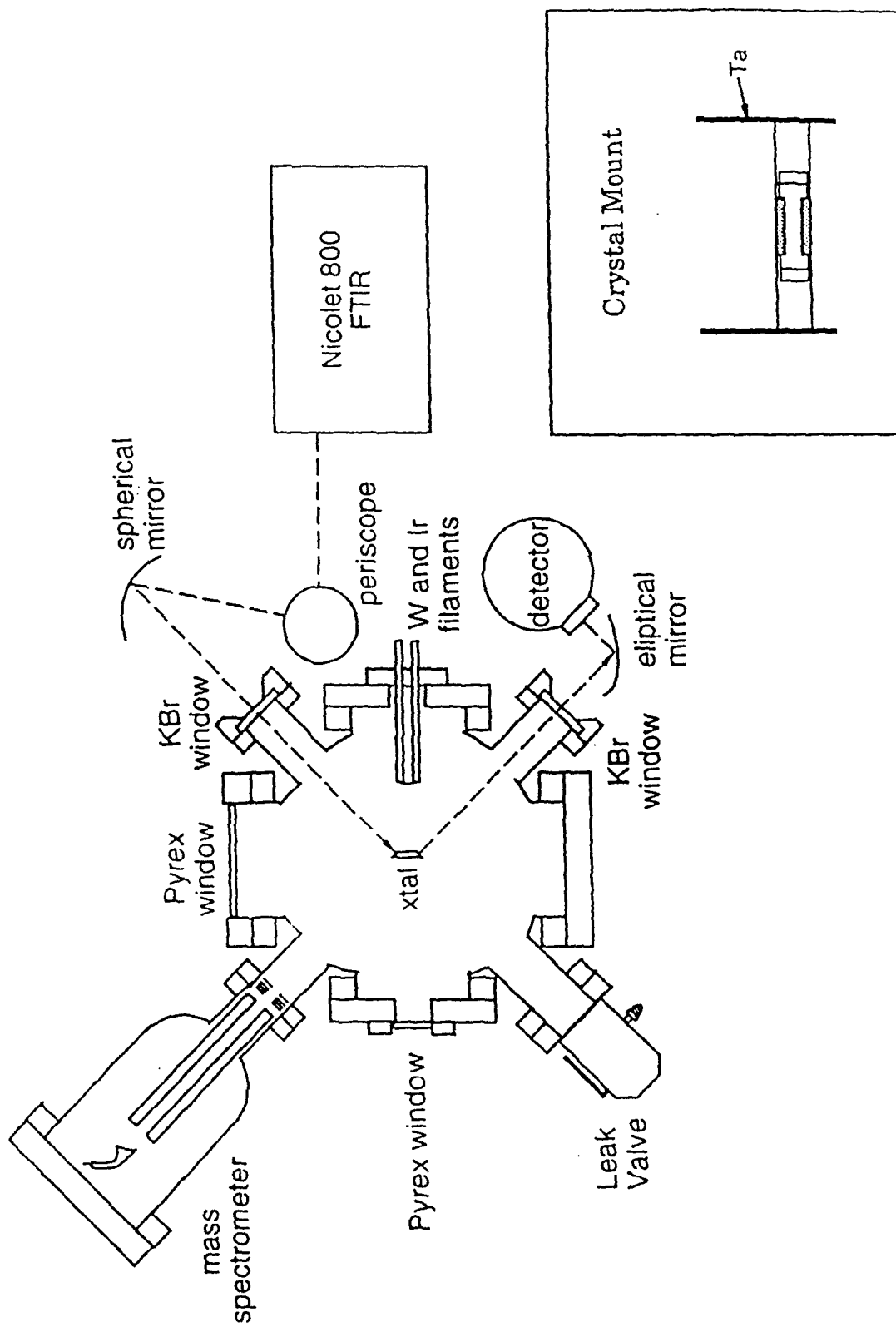


Figure 1. A schematic representation of the ultrahigh vacuum system used for multiple internal reflection infrared spectroscopy studies on diamond.

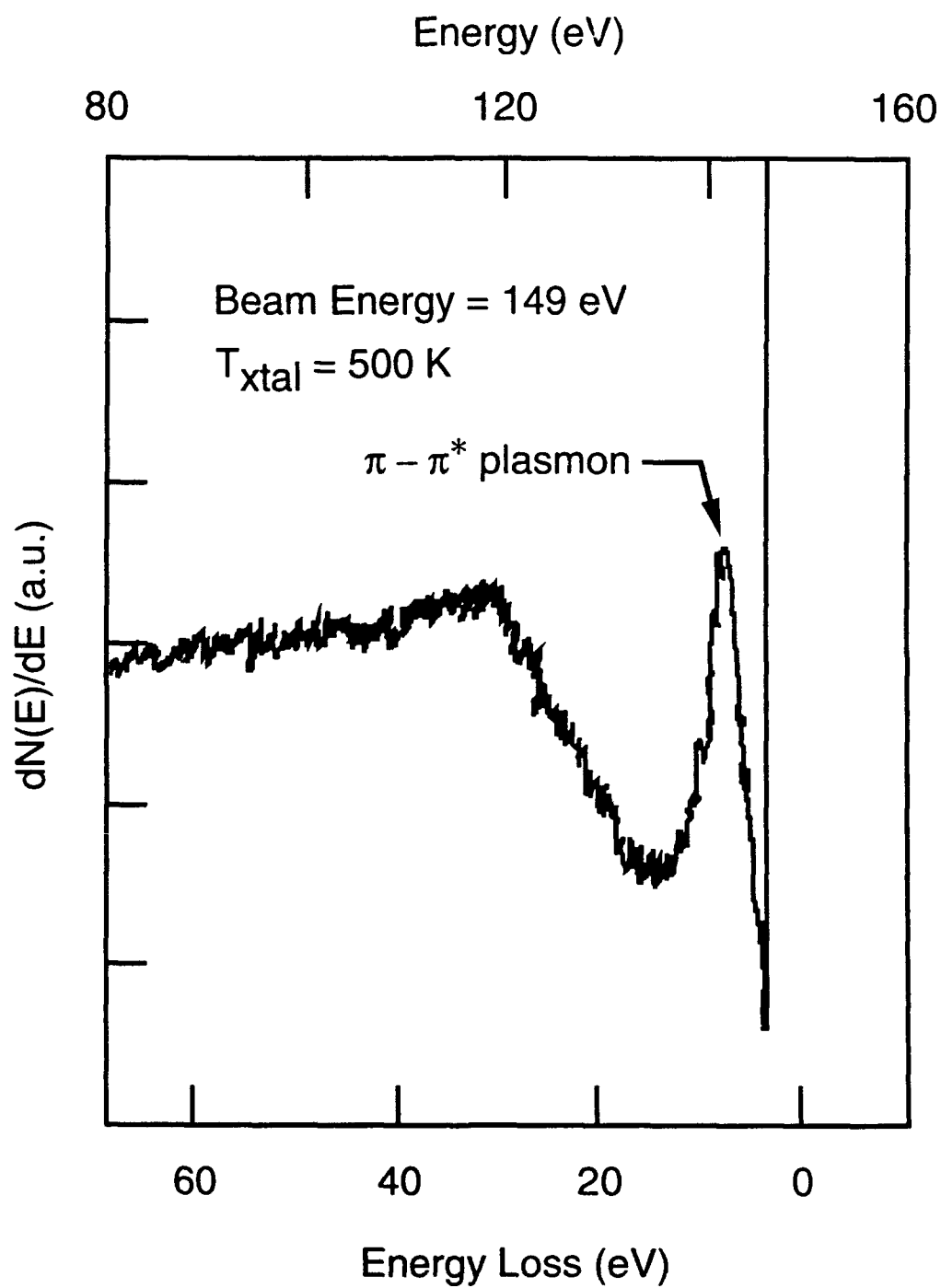


Figure 2. Post mortem electron energy loss spectrum (ELS) of the diamond MIR prism.

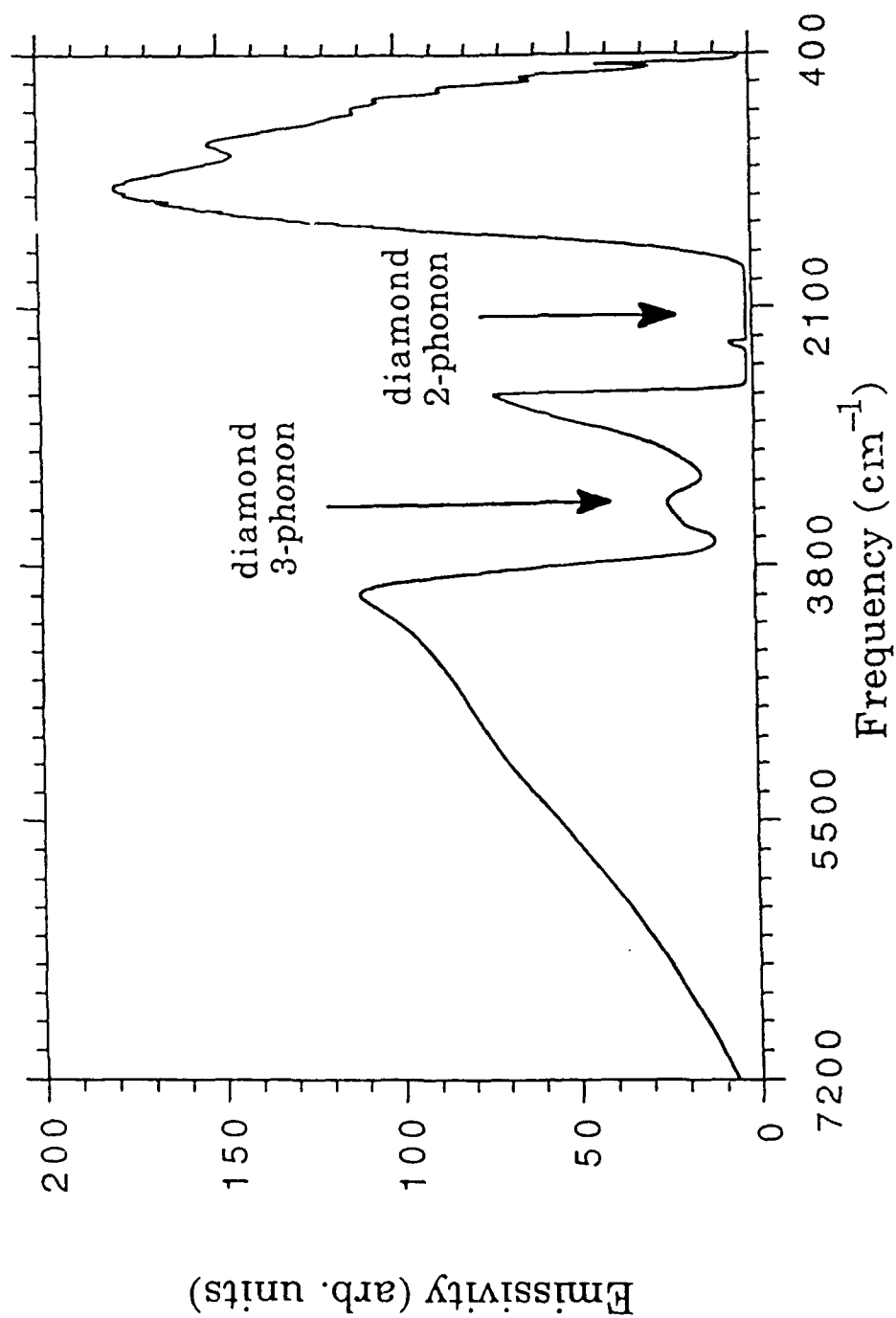


Figure 3. Single beam spectrum through the diamond(110) multiple internal reflection element.

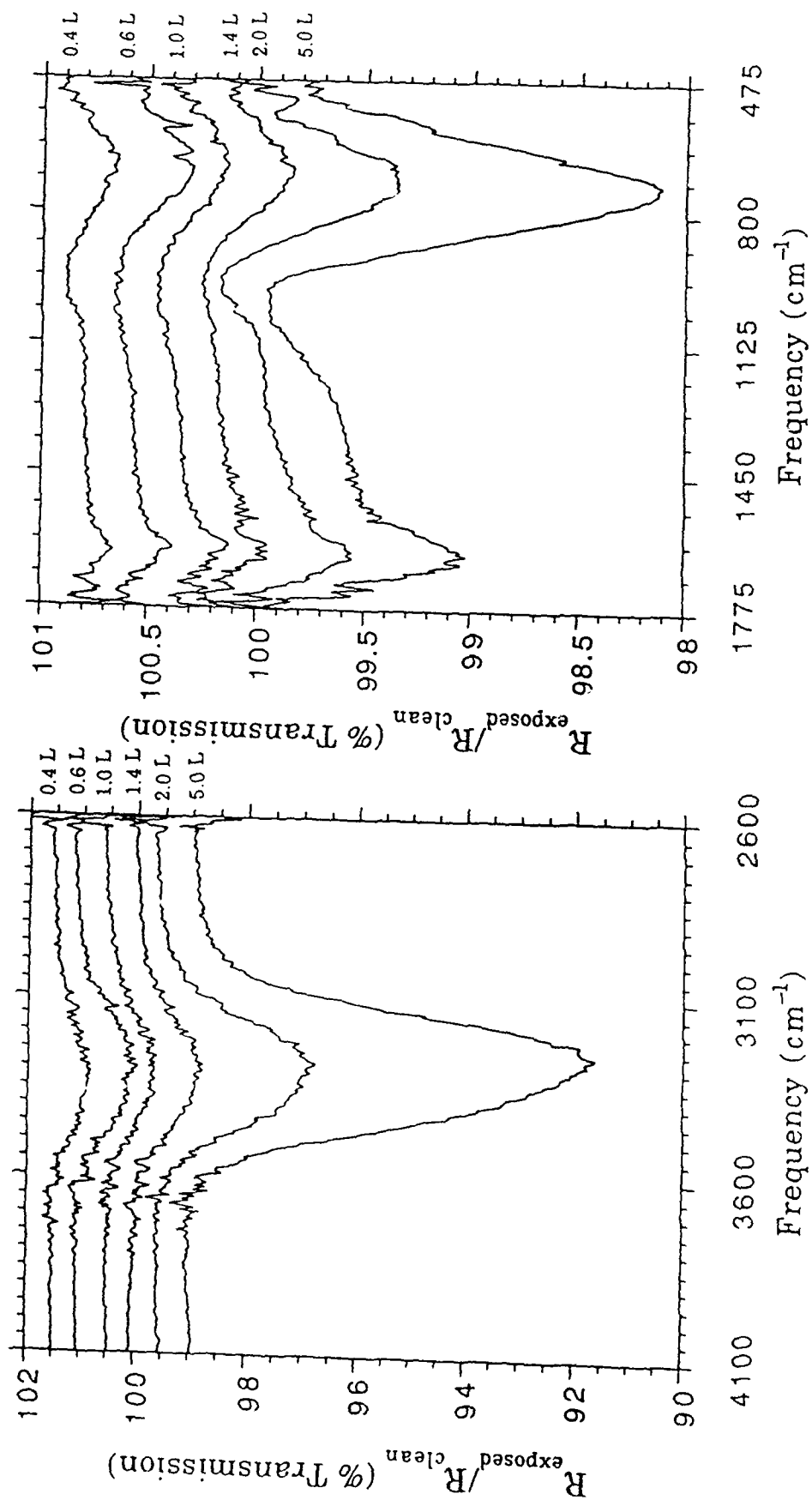


Figure 4. MIRIR spectra for a series of water exposures (0.4 L - 5.0 L) on the clean diamond(110) surface at 100 K. Spectra have been offset slightly from each other along the y-axis for clarity.

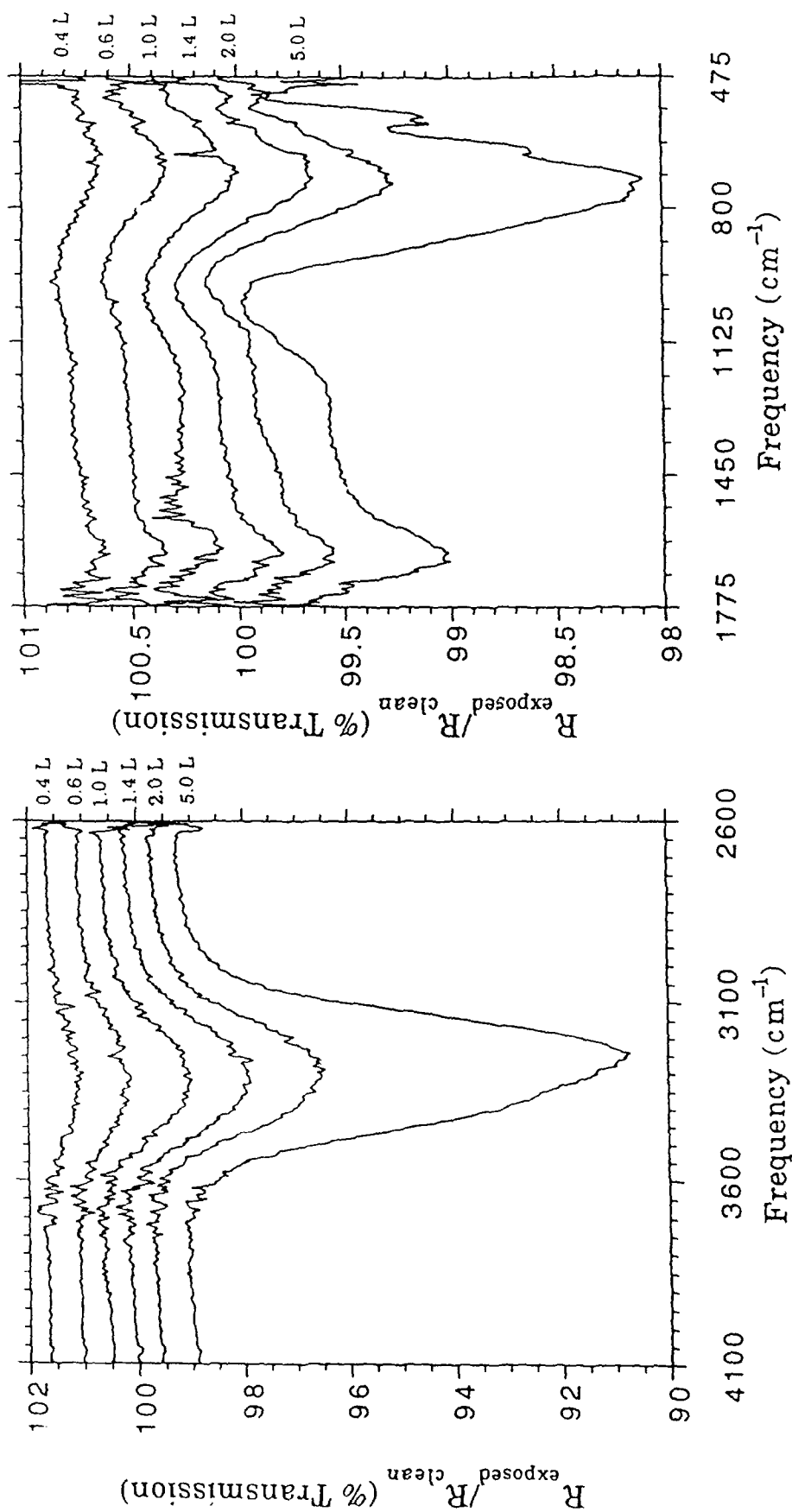


Figure 5. MIRIRS spectra for a series of water exposures (0.4 L - 5.0 L) on the hydrogen-terminated diamond(110) surface at 100 K. Spectra have been offset slightly from each other along the y-axis for clarity.